5

10

15

30

Claims

- 1. A non-aqueous well bore treatment fluid for selectively reducing the outflow of water during recovery of hydrocarbons from a hydrocarbon reservoir in a formation, the fluid containing 5 to 40 weight per cent of a water-immiscible dissolved compound based on α -branched carboxylic acid, derivatives or co-polymers thereof, and capable of forming a precipitate that is substantially soluble in hydrocarbons and substantially insoluble in water.
 - 2. A well bore treatment fluid according to claim 1, wherein the precipitate is soluble to at least 5.0 wt % in hydrocarbons.
- 3. A well bore treatment fluid according to claim 2, wherein the precipitate is soluble to at least 10.0 wt % in hydrocarbons.
- 4. A well bore treatment fluid according to any one of the preceding claims, wherein the precipitate is less than 1.0 wt % soluble in water.
- 5. A well bore treatment fluid according to claim 4,
 wherein the precipitate is less than 0.10 wt % soluble in water.
 - 6. A well bore treatment fluid according to any one of the preceding claims, wherein the melting point of the precipitate is over 50°C.
 - 7. A well bore treatment fluid according to claim 6, wherein the melting point of the precipitate is over 100°C.

- 8. A well bore treatment fluid according to any one of the preceding claims, which is solvent-based.
- 9. A well bore treatment fluid according to any one of claims 1 to 7, which is oil-based.
 - 10. A well bore treatment fluid according to any one of claims 1 to 7, which is based on a mixture of solvent and oil.
 - 11. A well bore treatment fluid according to any one of claims 1 to 7, which is based on a mixture of solvent and water.
 - 12. A well bore treatment fluid according to any one of the preceding claims, wherein the precipitate is a divalent or trivalent metal salt of an α -branched carboxylic acid.
- 20 13. A well bore treatment fluid according to claim 12, wherein the precipitate has the structure:

 $(R_1COO^-)_nM^{n+}$

wherein:

10

15

25

30

 R_1 is a C_{30} - C_5 aliphatic group having a C_{20} - C_4 linear chain bonded at a terminal carbon atom thereof (the α carbon atom) to the carbon atom of the carboxyl (COO) group, and further having at least one C_1 , C_2 or C_3 side group bonded to said terminal carbon atom, and

M is a divalent or trivalent metal cation.

14. A well bore treatment fluid according to claim 13, wherein two of said side groups are bonded to said terminal carbon atom.

WO 2005/035936 PCT/GB2004/004251 63

A well bore treatment fluid according to claim 13, wherein the precipitate has the structure:

 $(R_2COO^-)_nM^{n+}$

wherein:

 R_2 is a $C_{10}-C_{30}$ cyclyl group bonded at a carbon atom thereof (the α carbon atom) to the carbon atom of the carboxyl (COO) group, and having at least one C_1 , C_2 or C_3 side group bonded to the α carbon atom, and

M is a divalent or trivalent metal cation.

10

5

- 16. A well bore treatment fluid according to claim 15, wherein R2COO is an abietate group.
- A well bore treatment fluid according to claim 1, 17. wherein the compound is immiscible in a solvent fully 15 miscible with water.
 - A well bore treatment fluid according to claim 1, wherein the α -branched carboxylic acid is abietic acid.

20

30

- A well bore treatment fluid according to claim 18, wherein the precipitate is a divalent or trivalent metal salt of abietic acid.
- A well bore treatment fluid according to claim 18, 25 20. wherein the precipitate is polymerised abietic acid.
 - 21. A well bore treatment fluid according to claim 18, wherein the precipitate is a divalent or trivalent metal salt of polymerised abietic acid.
 - A well bore treatment fluid according to claim 18, wherein the precipitate is a phenolic co-polymer of abietic acid.

23. A well bore treatment fluid according to claims 1, wherein the dissolved compound is a divalent or trivalent metal salt.

24. A well bore treatment fluid according to claim 23, wherein the divalent metal is calcium, magnesium or zinc.

5

20

25. A well bore treatment fluid according claim 1, wherein said dissolved compound is a precursor, the precursor being degradable to form the carboxylate anion of a divalent or trivalent metal salt.

26. A well bore treatment fluid according to claim 1, wherein the precipitate has the structure:

27. A well bore treatment fluid according to claim 1, wherein the precipitate has the structure:

28. A well bore treatment fluid according to claim 1, wherein the precipitate has the structure:

5

10

15

20

- 29. A method of reducing the outflow of water during recovery of hydrocarbons from a hydrocarbon reservoir in a formation, comprising:
- (a) providing a well bore treatment fluid according to claim 1, and
 - (b) injecting said fluid into a well bore; and
- (c) letting the fluid permeate formation surrounding the well bore to reduce the outflow of water therefrom.
 - 30. The method of claim 29, comprising:
 - (a) providing a well bore treatment fluid according to claim 1, and
 - (b) injecting said fluid into a well bore; and
 - (c) letting the fluid permeate formation surrounding the well bore to form precipitates in the presence of water in the formation to reduce the outflow of water therefrom.

- 31. A method according to claim 29, wherein formation comprises a multi-layered reservoir with each layer having a flowpath into the wellbore.
- 32. A method according to claim 29, further comprising the step of injecting acid into the well bore.
- 33. A method according to claim 29, further comprising the step of injecting acid into the well bore after injection of the well bore treatment fluid.
 - 34. A method according to claim 29, further comprising the step of delaying precipitation.
- 35. A method according to claim 30, wherein precipitation is delayed by injecting a spacer fluid into the formation before the treatment fluid.
- 36. A method according to claim 29, further comprising:
 20 (d) injecting water or brine into the formation.

25

30

- 37. A method according to claim 36, wherein the steps of injecting of treatment fluid and injection of water or brine are repeated to enhance the blocking of water in the formation.
- 38. A method according to claim 29, further comprising the step of reversing flow direction in the well bore to resume hydrocarbon production.